

AD-A057 140

GENERAL ELECTRIC CORPORATE RESEARCH AND DEVELOPMENT --ETC F/G 11/2
LEAD ZIRCONATE TITANATE (LZT) CERAMICS.(U)

JUN 78 J H ROSOLOWSKI, R H ARENDT

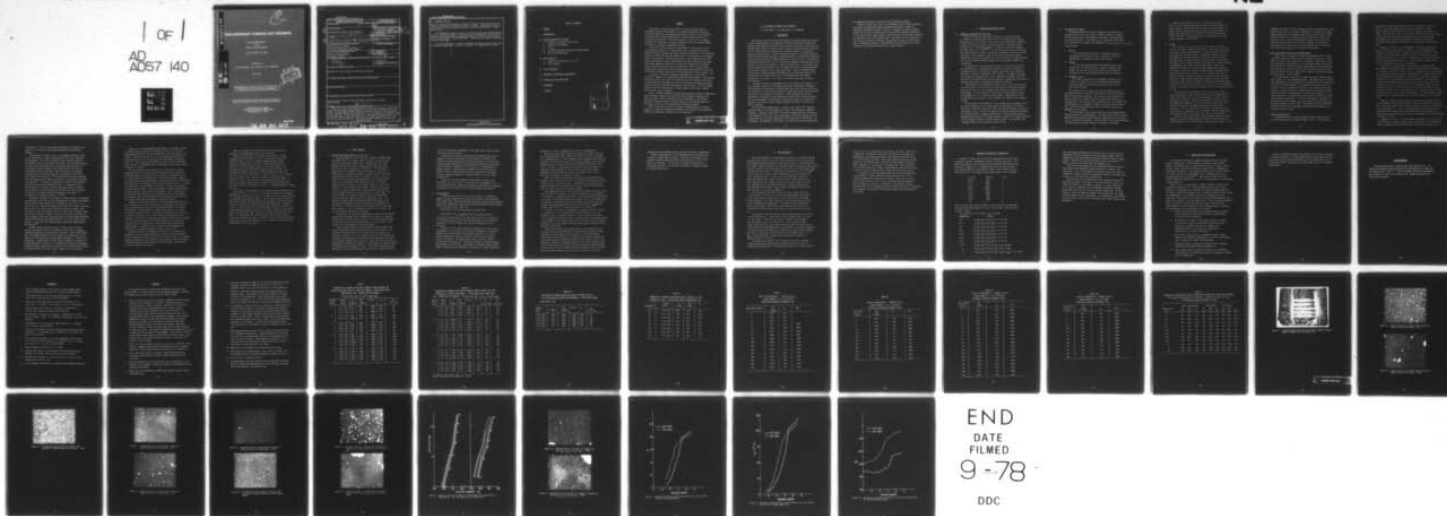
N00014-76-C-0659

UNCLASSIFIED

SRD-78-096

NL

1 of 1
AD
A057 140



END
DATE
FILMED
9-78
DDC

AD A057140

AD No. _____
DDC FILE COPY

11 na

LEAD ZIRCONATE TITANATE (LZT) CERAMICS

Annual Summary Report
to the
Office of Naval Research

Contract N00014-76-C-0659

Submitted by

J.H. Rosolowski, R.H. Arendt and J.W. Szymaszek

June 1978

DDC
RECEIVED
AUG 8 1978
F

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for public release; distribution unlimited

General Electric Company
Corporate Research and Development
Schenectady, NY 12301

SRD-78-096

78 08 04 027

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
LEAD ZIRCONATE TITANATE (LZT) CERAMICS		Annual Summary Report. 1 May 77 - 30 Apr 78
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER
J.H./Rosolowski, R.H./Arendt J.W./Szymaszek		SRD-78-096
9. PERFORMING ORGANIZATION NAME AND ADDRESS		8. CONTRACT OR GRANT NUMBER(s)
General Electric Company Corporate Research and Development P.O. Box 8, Schenectady, N.Y. 12301		N00014-76-C-0659
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Office of Naval Research Metallurgy Program Office Arlington, VA 22217		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE
(12) 49p.		June 1978
		13. NUMBER OF PAGES
		45
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Lead Zirconate Titanate, Powder Synthesis, Piezoelectric Ceramic, Aging, Poling		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Tests of batch-to-batch reproducibility of LZT powders made by molten salt synthesis were carried out by measuring the properties of ceramics fired from them. Individual post-poling dielectric constants and planar coupling coefficients lay within 94% and 97%, respectively, of the average of all samples fired in the same way. Striking similarities in characteristic aging behavior of the dielectric constant among all samples from all powder batches that were fired in the same way were observed. The characteristics changed with the firing</p> <p>(Continued on back)</p>		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

406 617 78 08 04 027

LB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. ABSTRACT (cont'd)

method. Tests of poling behavior indicate an effect of post-firing history on properties achieved in subsequent polings of a sample. The presence of unreacted zirconia in the starting powder was found to be deleterious to ceramic properties.

The post-poling dielectric constant of some Cr containing compositions was found to experience a sudden, rapid increase of sometimes more than 100% about 120 days after poling with no accompanying changes in planar coupling coefficient or piezoelectric strain coefficient. The dielectric constant subsequently decreased with time.

No significant effect on ceramic properties or aging was found after cyclic hydrostatic compression of a number of different LZT compositions to 69 MPa.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

TABLE OF CONTENTS

SUMMARY

- I. INTRODUCTION
- II. POWDER REPRODUCIBILITY TESTS
 - A. Comments on Analysis for Pb in LZT
 - B. Description of Powders
 - C. Firing
 - D. Post-Firing Sample Preparation and Measurement
 - E. Results and Discussion
- III. AGING BEHAVIOR
 - A. Powders from Batches A, B, C, D, E
 - B. Other Powders
- IV. POLING BEHAVIOR
- V. RESPONSE TO HYDROSTATIC COMPRESSION
- VI. CONCLUSIONS AND FUTURE WORK

REFERENCES

APPENDIX

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
ODC	Bull Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUL 1 1971	
BY	
DISTRIBUTION/AVAILABILITY CODES	
SPECIAL	
A	

SUMMARY

This report covers the second year's work on a program aimed at developing a better understanding of the mechanisms whereby the methods of powder preparation, processing and sintering control the microstructure of lead zirconate titanate(LZT)ceramics as well as their electric and piezoelectric properties. The work is based on the use of the technique of molten salt synthesis to produce homogeneous, fully reacted LZT powders from which the ceramics investigated are made.

A test of the batch-to-batch reproducibility of the powder, made by measuring the properties of ceramics made from it, showed that the post-poling dielectric constants and planar coupling coefficients of the individual samples lay within $\pm 4\%$ and $\pm 7\%$, respectively, of the average for all samples fired in the same way. Striking similarities in the aging behavior of the relative dielectric constant, specifically the rates of aging and the times when sudden changes in aging rate occurred, were observed in all samples from all batches that were fired in the same way. These characteristics changed with firing method. No such similarities were observed in the aging of the planar coupling coefficient or the piezoelectric strain constant, d_{33} .

An unusual, previously unreported aging behavior of the relative dielectric constant of Cr containing compositions was observed. This parameter decreased by about 1% in about the first 120 days after poling, after which a rapid increase of sometimes more than 100% occurred, followed by a general decrease with time interrupted by smaller, rapid increases. The loss tangent behaved in much the same way, but no unusual aging of the planar coupling coefficient or d_{33} was observed.

Tests of ceramic properties achieved when poling at different temperatures, and/or different poling fields, and/or different methods of applying the field were made. There was evidence that the magnitude of the relative dielectric constant achieved on poling depends on the previous history of the sample, even if it had previously been completely depoled.

Tests of the effect of cyclic hydrostatic compression up to 69 MPa of samples of a number of compositions indicate little effect on the properties measured at atmospheric pressure or on the aging rate.

PRECEDING PAGE BLANK

LEAD ZIRCONATE TITANATE (LZT) CERAMICS

J. H. Rosolowski, R. H. Arendt and J. W. Szymaszek

I. INTRODUCTION

This report covers the second year's work on a program aimed at developing a better understanding of the mechanisms by which the methods of powder preparation, processing and sintering control the microstructure of lead zirconate titanate (LZT) ceramics as well as their electrical and piezoelectric properties. The first objective of the program was to develop a method, of potentially commercial practicability, by which homogeneous powders of controlled stoichiometry could be produced, and whose sintering behavior as determined by measuring ceramic properties would be highly reproducible from lot to lot. This objective was deemed necessary since one of the practical problems encountered when making piezoelectric LZT ceramic bodies to rigid specifications is the variability in results obtained from different lots of powder made by the conventional method of calcining a mixture of the constituent oxides. Since no reliable method now exists for characterizing an LZT powder so as to accurately predict the properties of the ceramic fired from it, obtaining powders that behave reproducibly is necessary for a study of the effects of powder processing and sintering.

The method chosen for development was that of molten salt synthesis. In this technique, reaction of the constituent oxides (or precursor compounds that decompose to the oxides on heating) takes place while they are dissolved in a molten salt, rather than by solid-state diffusion between contacting oxide particles as in conventional calcination. This technique holds out the possibility of producing a more homogeneous and more fully reacted LZT powder than that obtainable by conventional calcination because of the effectively greater area of mutual contact between particles and greater reaction rate that it provides.

The first Annual Summary Report of work on this contract⁽¹⁾ contains a detailed account of the development work done on the molten salt synthesis technique. Briefly, it was shown that reactive powders could be so made over a wide range of Zr/Ti ratio, and a large number of different dopants could be incorporated into the basic compositions both singly and in combination. For convenience, the Appendix to this report also gives step-by-step instructions

for making an LZT powder by the molten salt synthesis technique.

During the first year's work, the attainment of good ceramic properties when using a standardized sintering procedure was used as a guide to developing the powder synthesis technique. Although the results obtained towards the end of the reporting period indicated that powders synthesized by the same procedure would produce ceramics having closely similar properties, no controlled test of this had been made. This report of the second year's work will be principally concerned with giving the results of such tests as well as showing the effects of some different firing conditions on ceramic properties, and reporting observations on aging behavior.

II. POWDER REPRODUCIBILITY TESTS

A. Comments On Analysis For Pb In LZT

Lead is a volatile constituent in LZT and it is well known that its content in the powder and ceramic must be controlled if the desired properties are to be attained. This is usually accomplished in commercial practice by firing the ceramic in closed containers containing pellets of PbZrO_3 or of a PbO-PbZrO_3 mixture to establish a PbO vapor pressure and thus prevent loss of PbO ^(2,3). In the work reported here, the pressed discs were buried in a powder of their own composition and fired in closed containers. Discs weighing 5 grams fired this way typically showed a weight loss of around 0.6 percent, part of which was due to slight chipping that occurred when the adhering powder which had hardened somewhat was scraped away.

The possibility of making high precision, direct analyses for Pb in LZT was looked into. Discussions with analytical chemists yielded the information that the available wet chemical techniques could probably be developed to yield an uncertainty of ± 0.3 percent. An inquiry directed to the analytical department of a major commercial LZT powder supplier⁽⁴⁾ produced the information that they had developed a proprietary wet chemical technique which gave an uncertainty of about ± 0.1 percent.

The possibility of measuring Pb contents using X-ray fluorescence was also looked into. Differences in the lead content of different specimens accurate to 1 part in 2 or 3 thousand could probably be measured but the large number of counts required for such accuracy would require tying up the equipment for 2 or 3 days for each specimen. Determination of the absolute Pb content would, of course, require that highly precise standards be made.

In the light of the foregoing, it was decided that the probable value of precise information on the lead content of LZT powders and ceramics would not at this time justify the effort and expense required to obtain it. Accordingly, control of the lead content was effected through standardizing the excess lead used in powder synthesis and by firing the same number of pressed discs along with a constant quantity of powder of the same composition in each closed, stabilized zirconia firing crucible. The crucibles were "seasoned" before use by firing LZT powder in them.

B. Description Of Powders

Experiments designed to show the degree of reproducibility of ceramic properties were made using 5 different batches of powder. The identifying letter and comments on the powder synthesis method used are given below. In all batches, the constituents were mixed in the proportions to produce the composition, $\text{Pb}_{.94} \text{Sr}_{.06} (\text{Zr}_{.53} \text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$.

1. Batch A

A 2 kg batch made according to the method outlined in the Appendix except that the use of a blender to break up agglomerates as described in step 1 was omitted.

2. Batch B

A 1 kg batch whose preparation included the use of the blender only for the ZrO_2 slurry. A small, stainless steel blender jar was used only for this batch and a slight discoloration of the slurry indicated that some wear occurred.

3. Batches, C, D, E

All made as described in the Appendix including use of blender on a slurry of all the constituents mixed together. A larger blender jar was used and no discoloration of the slurry was observed.

Two weight percent of stearic acid was incorporated into the as-prepared powders in order to achieve better particle packing and green strength during pressing. The stearic acid was dissolved in benzene, added to the powder and the resulting slurry milled in a polyethylene jar for 24 hours using zirconia balls. The milling time used happened to be convenient, a shorter time would have served as well. The milling procedure also serves to further break-up any aggregates in the powder.

The milled powder slurry was poured into an open beaker and the benzene evaporated by applying heat. The powder was stirred constantly during drying to prevent stratification or segregation of the stearic acid as the benzene evaporated. The dry powder was then passed through a 60 mesh nylon screen after which it was ready for pressing.

Samples were pressed in a 2.54 cm diameter Carboloy die. About 5 g of powder was loaded and pressed at 69 MPa (10 Kpsi) for about 1 minute. This yielded discs of about 2.5 mm thickness. In order to insure uniform density, these discs were then placed in a rubber bag, immersed in oil, and isostatically pressed at around 340 MPa (50 Kpsi). The green densities of bodies pressed in this way were around $5.7 \times 10^3 \text{ Kg/m}^3$.

C. Firing

The pressed discs were fired in air for one hour at 600°C to burn off the binder. Two different kinds of firings were then made to determine powder reproducibility. In the first kind, 5 discs of each batch were stacked in separate stabilized zirconia crucibles with powder of the same composition around and between the discs. The same amount of powder was used in each crucible. The crucibles were about 4 cm in internal diameter and depth and had been "seasoned" by previously having been fired with LZT powder in them. The crucibles were then covered with seasoned alumina discs placed so as to leave a small gap so that the oxygen furnace atmosphere would more easily permeate the contents. All 5 crucibles were placed inside a covered, seasoned, stabilized zirconia box which had a gas inlet port. This box was flushed with oxygen and then placed into a box type furnace heated by Globars. An oxygen flow was maintained through the zirconia box at about $9.3 \times 10^{-3} \text{ m}^3/\text{h}$ (0.1 cfh) throughout the run. The oxygen flow into the furnace was kept at around $0.28 \text{ m}^3/\text{h}$ (3 cfh).

The temperature-time schedule for the first kind of firing was; a temperature increase rate of 85°C/h from room temperature to 850°C, then 130°C/h up to the firing temperature of 1325°C, which was held for one hour. The power to the furnace was then cut and the temperature dropped 330°C in the first hour, then 130°C, 100°C and 80°C in the next three hours respectively and more slowly thereafter. The box containing the crucibles was removed from the furnace when its temperature was around 200°C. Furnace temperatures were measured with a thermocouple placed near the zirconia box.

In the second type of firing, discs from each powder batch were placed in crucibles as previously described, but each crucible was fired separately in a specially built, closed-end tube furnace. After

flushing, the oxygen flow rate through the furnace was maintained around $0.028 \text{ m}^3/\text{h}$ (0.3 cfh). The furnace temperature, as measured by thermocouples located near the crucible, went up at the rate of about $200^\circ\text{C}/\text{h}$ from room temperature to 1260°C , where it was held for 1 hour, then reduced at a rate of about $200^\circ\text{C}/\text{h}$ down to where the controller was turned off (about 200°C) and the furnace allowed to cool naturally. The firings in the tube furnace could be done much more rapidly than in the box furnace because of its smaller thermal mass.

D. Post-Firing Sample Preparation And Measurement

After firing, the powder surrounding the samples formed a weakly bonded mass which was removed from the crucible in one piece. Figure 1 shows one of these pieces with some of the powder scraped away to show the encapsulated, sintered discs. The surrounding powder was scraped away from the discs and their density determined by water displacement. They were then ground flat on both sides on 600 grit silicon carbide paper and silver electrodes (Dupont 7713 conductor composition) painted on and fired for 1 hour at 600°C .

The capacitance of each disc was then measured at 1000 Hz using a General Radio Co. 1615 Capacitance Bridge. The samples were then poled while immersed in a bath of Fluorinert (3M Company) at 120°C by applying a field of 2.36 MV/m ($60\text{V}/\text{mil}$) for 3 periods of 5 minutes each with reversal of direction between the periods. The capacitance was again measured at various times after poling along with the planar coupling coefficient, which was determined by the resonance technique⁽⁵⁾. The relative dielectric constant was calculated from the sample dimensions and the measured capacitance. After the instrument was obtained, the piezoelectric strain constant, d_{33} , was measured with the Berlincourt d_{33} Meter (Channel Products, Inc). Some samples were also examined in the optical microscope to determine the grain size and general microstructural characteristics.

E. Results And Discussion

The values obtained from measurements made on ceramics fired in the two different ways are shown in Tables I and II. The tabulated

values are the pre-poling relative dielectric constant at 1 KHz (K_o) and the 1 day post-poling values of relative dielectric constant (K_{33}^T) and loss tangent ($\tan \Delta$) at the same frequency, the planar coupling coefficient (k_p), and the piezoelectric strain constants d_{31} and d_{33} . d_{31} was calculated from the resonance frequency and the other data. Some samples were broken during handling or showed strong multiple resonances after poling and therefore were not included in the measurements.

Figures 2a, 2b and 2c are micrographs of a ceramic specimen from batch C fired in the box furnace. Figure 2a is a low magnification picture of a polished surface showing large pores in the ceramic. The presence of such large pores, which account for a significant fraction of the total porosity of the piece, is typical of all ceramics made from molten salt synthesized powders. It is also typical of ceramics made from calcined powders that have been examined.

Figure 2b is a higher magnification view of a polished section. The rounded precipitate particles visible there are ZrO_2 which is present to the extent of about 0.4 volume percent, as determined from a micrograph. This is considerably more than the approximately 0.03 volume percent present in an as-made powder prepared with the inclusion of the step of passing a slurry of the reactant powders through a blender⁽¹⁾. The additional zirconia was undoubtedly picked up from wear of the zirconia balls used to mix in the stearic acid by milling. For comparison, Figure 3 shows a polished section of a ceramic from batch A for which the omission of the blending step would lead to the expectation of a zirconia content of about 0.5 volume percent in the powder before milling. It would therefore appear that there is a significant amount of ball wear occurring in the milling step.

Figure 2c shows the grain boundaries revealed on a polished section after treatment with a boiling, 5% HCl solution containing a few drops of HF. The average grain sizes of ceramics from all 5 batches in this firing lie in the range $3.7 \pm 0.2 \mu m$. The average grain size was obtained by determining the average distance between successive points where grain boundaries cross a straight line drawn on a micrograph, and then multiplying the result by 1.5⁽⁶⁾.

Figures 4a, 4b and 4c are the analogues of Figures 2a, 2b and 2c for ceramics fired from batch C powder in the tube furnace. The average grain sizes of ceramics from batches B through E fired in that furnace lie in

the range $2.6 \pm 0.2 \mu\text{m}$. The average grain size of the ceramic from batch A is $1.6 \mu\text{m}$ but the grain size distribution is distinctly bimodal.

Turning again to Tables I and II, one readily noticeable result is the difference in ceramic density obtained by the two different firing methods. This can be attributed to the different amount of grain growth that occurred during the firings. The more rapid heat-up and lower peak firing temperature experienced during firing in the tube furnace tended to suppress grain growth during the critical, intermediate stage of sintering. Thus, the amount of sweeping-up and coalescence of pores by moving grain boundaries was less than for firings in the box furnace. This resulted in the pores remaining small and thus being more quickly removable by the diffusion processes of sintering⁽⁶⁾. The result is graphically evident in the different pore distributions seen in Figures 2a and 4 a. Comparison of the other properties of ceramics from the same powder batch in Tables I and II reveals no obvious systematic difference that may be ascribed to the grain size and/or density difference in this range, in accord with the findings of Webster, et al⁽⁸⁾.

The density achieved in both types of firings, however, is dependent to some degree on the fact that the atmosphere in the furnace was oxygen, which can more easily diffuse out of closed pores than can air. To illustrate, four samples made from batch A powder were fired as described above in the tube furnace using flowing air instead of oxygen. The densities of these four samples lay in the range $7.620 \pm 10 \text{ Kg/m}^3$, which is less than achieved in oxygen. This effect had been noted before in other firings of molten salt synthesized LZT of various compositions made during the experiments performed during the first year's work on this contract. It has also been observed during commercial fabrication of LZT ceramics⁽⁹⁾.

Another readily noticeable result in Tables I and II is that ceramics from powder batch A have uniquely low dielectric constants, coupling coefficients and piezoelectric constants. This is very likely due to the higher unreacted zirconia content in this batch due to the omission of the blending step during powder preparation. To check this hypothesis, 1 weight percent of ZrO_2 powder was added to a quantity of as-made LZT powder from batch E. It was then put through all subsequent preparation steps, starting with the addition of stearic acid by milling, and discs pressed from it were fired in oxygen in the tube furnace.

Figure 5a is a low magnification photograph of a polished section of ceramic which shows the pore structure, and Fig. 5b is taken at higher magnification to show the distribution of the ZrO_2 phase in the ceramic. The grain size was $2.6\ \mu m$. The pre-poling and 1 day post-poling properties of the 5 discs fired from this powder are given in Table III. These properties are similar to those of batch A ceramics given in Table II and indicate that a considerable degradation of batch E powder has occurred.

One can speculate on the possibility of a difference in powder homogeneity arising from zirconia aggregates that do not fully react during synthesis in the molten salt as opposed to inhomogeneities due to zirconia particles introduced into a well reacted powder. However, such subtleties are beyond definitive verification by analytical techniques. The results obtained do, however, indicate the possibility that, on a weight for weight basis, zirconia which is present as a result of incomplete reaction during synthesis is more deleterious to ceramic properties than zirconia introduced into a well reacted powder. This is indicated by the fact that the ceramics made from powder batch E with 1 w/o added zirconia have about the same properties as those made from batch A, but they contain about twice the amount of unreacted zirconia.

Finally, the principal objective of the experiments from which the data in Tables I and II were obtained was to demonstrate the batch to batch reproducibility of molten salt synthesized powder. The results are equivocal. Considering the ceramics from batches B, C, D and E, the reproducibility of density and ceramic microstructure for each type of firing is excellent. Also, in each firing, the variation of the averages of the dielectric constants and coupling coefficients for samples from each batch as compared to the grand average for all batches is within $\pm 4\%$ and $\pm 7\%$, respectively. These values also represent good reproducibility as compared to what could have been expected from a random group of commercial powders a couple of years ago⁽⁹⁾.

However, except for those made from batch E, it is apparent that samples from the same powder batch did not achieve the same absolute, or relative, degree of poling after the two kinds of firing. For instance, samples from batches B and D poled well after firing in the box furnace, but relatively poorly after firing in the tube furnace. The converse is true for samples from batch C.

There is evidence that these variations are related to the different firing temperatures used in the two runs.

During the development of the tube firing furnace, a firing technique was used in which the furnace tube was horizontal and contained a short section of alumina tubing which was loosely capped with alumina discs at each end. The LZT discs were set one-high on a zirconia sagger inside the tube with powder of the same LZT composition piled loosely underneath and over them. This technique was abandoned because it became apparent that lead loss from this set-up was erratic and the density variations in the ceramics were unacceptably large. However, a number of firings were made of samples from batch C in which the firing temperature was 1320°C, i.e. that of the samples shown in Table I, while the firing schedule was the same as that for the samples in Table II. Firings were made in oxygen and in air.

The results of measurements of the ceramics made in 8 different runs are given in Table IV. It is to be noted that the dielectric constants and coupling coefficients are similar to those for the box furnace firing of this powder batch shown in Table I, rather than to those in Table II. This result implies that the different poling behavior revealed in those Tables are caused by the different firing temperature used. However, so far no correlation has been observed between the small variations in powder synthesis, powder preparation, pressing or firing of these samples and the other batch-to-batch and sample-to-sample variations described above. It would appear that additional data from several firings of samples made from the same batch of powder as well as data on post-poling properties versus firing temperature will be required to help develop an understanding of what is going on.

III. AGING BEHAVIOR

A. Samples From Powder Batches A, B, C, D, E

The aging behavior of the dielectric constant of samples made from powder batch C is shown in Figs. 6a and 6b for firing in the box and tube furnaces, respectively. Straight lines were drawn between successive data points, which are not shown, but whose positions in time are indicated by asterisks. The similarity in aging behavior of samples from the same firing is to be noted. Furthermore, the similarity extends to samples from all the other powder batches that were fired in the same way. That is, for all samples fired the same way and regardless of batch, the points in time (on the logarithmic scale) where the slopes of the lines change are closely similar to those shown in Fig. 6, as are the slopes of the lines between those points. The plots of k_p versus $\log(t)$ for samples from the same firing and made from the same batch of powder show only a general similarity to each other. On the other hand, no distinctive change in curve characteristics occurs at the times when the curves for K_{33}^T change slope. The curves for samples made from different powders but fired in the same way also show only a general, nondistinctive similarity to each other. No curve feature peculiar to samples fired in the same way is apparent. Also, no significant change in loss tangent with time at 1 KHz was observed in any sample.

Incidentally, all property measurements on LZT discs are routinely preceded by measurements on two standard discs, made from commercial powder, which had been poled 4 years ago. These standards have shown a random variation of k_p and K_{33}^T within $\pm 1\%$ over the period of time covered by the measurements now being discussed.

These results indicate a strong similarity between samples made from the same powder when fired in the same way, with respect to the operation of those specific factors that control the aging of the dielectric constant. It is also apparent that, for these samples, the details of the aging process for dielectric constant depend strongly on the firing schedule used to make the ceramic, but very little on the magnitude of the dielectric constant or on the degree of poling achieved (as indicated by the magnitude of k_p). The results also indicate that the factors controlling the aging of k_p operate in a generally similar

way in all the samples, regardless of the powder batch they were made from or how they were fired.

Poling is the process of preferentially orienting ferroelectric domains in the LZT crystallites, which results in a change in the dielectric constant and planar coupling coefficient of a ceramic body. The post-poling relaxation of those properties toward their pre-poling values (aging) is thought due to the process of re-randomizing the domain structure. This process is thought to be influenced by the specific domain structure obtained and its associated inter-domain stresses, and on the build-up of trapped charge at, or near, grain boundaries⁽¹⁰⁾.

Because of the observations described above, and those to be described in the next section, we believe that the magnitude of the post-poling dielectric constant of LZT and its time behavior is strongly influenced by some factor or factors besides domain reorientation.

B. Other Powders

During the first year of work on this contract, a considerable number of powder compositions were made and ceramics fired from them. These samples have since been routinely measured to monitor aging behavior. Among those compositions were two that had been reported in the literature to have low aging rates. These are:

Composition 1; $\text{Pb}(\text{Zr}_{.52}\text{Ti}_{.48})_{.97}\text{Fe}_{.01}\text{Cr}_{.02}\text{O}_3$, and

Composition 2; $\text{Pb}_{.94}\text{Ca}_{.05}\text{Mg}_{.01}(\text{Zr}_{.52}\text{Ti}_{.48})_{.97}\text{Fe}_{.01}\text{Cr}_{.02}\text{O}_3$.

(In the first Annual Report⁽¹⁾ it was pointed out that the solubility of Ca and Mg is actually much less than that shown in the formula for Composition 2, which is written for the batch composition of the reactants.)

Tables V, VI, VII and VIII show data obtained from two different firings made in a box furnace with an oxygen atmosphere. The firing schedule was as described for that furnace in Section II-C except that the samples were held for 3 hours at 1225°C in one run and at 1275°C in the other. The samples were fired in covered crucibles as described in Section II-C. They were electroded, poled and measured as described in Section II-D. The behavior of the data shown in these Tables is typical of that obtained on all samples of these compositions

examined, i.e. three of composition 1 and six of composition 2.

These data show a small decrease in dielectric constant occurring out to around 100 days after poling, after which it starts to increase at an increasing rate to reach a high peak value sometime between 200 and 250 days. The dielectric constant then tends to decrease with time, but sudden increases to values less than that achieved in the first peak occur. The onset of the increase in dielectric constant appears to be preceded by the beginning of a large increase in the loss tangent. Subsequent changes in the value of the loss tangent occur in time phase with the changes in dielectric constant.

While the changes are occurring, the planar coupling coefficient changes little until the time of the first dielectric constant peak, when a decrease of a few percent occurs. Subsequently, small positive and negative changes occur at times which are not strongly correlated with those at which the dielectric constant changes.

Such aging behavior has not previously been reported for LZT, or any other piezoelectric ceramic. Its cause is unknown but it is suspected to be related to changes occurring near or at grain boundaries rather than in the bulk of the crystallites of the ceramic. Also, it is thought that the presence of chromium in these compositions is important since only chromium containing compositions have shown the effect. Chromium is commonly added to LZT if low aging properties are desired⁽¹¹⁾.

Figures 7a and 7b are micrographs of a polished section of ceramic of composition 1. The average grain size of this sample is 3.2 μm . Besides the large, rounded precipitates of ZrO_2 , there are also some large, elongated precipitates present. Analysis with a microprobe produced no detectible Fe or Cr signal in the bulk of the grains or at the grain boundaries, but large signals from these elements were obtained from the elongated precipitates.

These aging results lend strong support to the hypothesis given previously that the aging behavior of the dielectric constant in these specimens is not just due to the relaxation of a preferred domain orientation. This concept may also apply to LZT ceramics produced from other than molten salt synthesized powders, since erratic aging of the dielectric constant is frequently observed, as are uncorrelated changes in dielectric constant and planar coupling both during aging and poling. Thus the effects seen in ceramics made from composition 1 and 2 powders may differ only in degree, but not in kind, from those seen in LZT

ceramics made from different powders and having different compositions.

Further investigations of this phenomenon are being pursued, but a supply of samples must be assured. Therefore, more powder of composition 1 has been made and ceramics have been fired to see if the effect will reproduce. In addition, an attempt is being made to accelerate the onset of the increase in dielectric constant by aging at elevated temperature.

IV. POLING BEHAVIOR

The erratic behavior of the dielectric constant of LZT ceramics during aging was also evident in the early results obtained in an investigation of poling behavior which was begun in this contract period. The study was done on a simple ceramic disc made from the batch E powder described in Section II-B and which was fired in the tube furnace as part of the reproducibility study discussed in that section. The density of the sample was $7.77 \times 10^3 \text{ Kg/m}^3$ and its dielectric constant, after firing-on the silver electrodes but before poling, was 1042. In the course of the subsequent work this sample was depolarized 5 times by slow heating to 625°C , holding for 1 hour, followed by slow cooling. The value of d_{33} was always zero after this treatment but the successive dielectric constants obtained were 839, 900, 906, 918 and 928. Clearly, then, the specimen could not have been restored to its original condition.

Two bath temperatures were used in the poling study. They were 120°C and 140°C . For the test at 120°C the depoled sample was repoled in the same direction along the disc axis at successively increasing field strength by 3, 5 minute applications of the field with reversal of direction between each application. The properties were measured 20 minutes after poling. The sample was not depoled until after being poled with the highest field. The results are shown in Figs. 8, 9 and 10.

The poling at 140°C was done by 15 minute applications of the field in one direction only. These results are also shown in Figs. 8, 9 and 10. They show, as expected, that poling at higher field strengths produces higher values of k_p , K_{33}^T and d_{33} . Also, at high fields, a larger value of k_p and d_{33} is achieved when the field is reversed during poling instead of being maintained in one direction. The higher temperature of poling increased the change in k_p and K_{33}^T at the lower field strengths but was not as effective as field reversal at the higher fields. For K_{33}^T , on the other hand, a higher poling temperature resulted in a greater change at all fields.

In neither case, however, did the change in dielectric constant from the pre-poling value equal that obtained one hour after the first poling of this sample (281) as described in Section II-D. Neither did the

values of k_p and d_{33} reach those first values, which were .539 and 279, respectively. Furthermore, some data (not shown in the figures) was obtained from this sample by poling at 120°C with no field reversal up to a field of around 1.6 MV/m. This data shows the dielectric constant starting at 906 and generally following the curve shown for poling at 140°C. The data for d_{33} and k_p , on the other hand, follow the curves for the 120°C poling up to around 1.2 MV/m where a rapid increase occurs so that at around 1.4 MV/m the data follows the 140°C poling curves.

It therefore appears that depoling did not bring this sample back to the condition it was in before the first poling in spite of the complete disappearance piezoelectric activity. There also, as noted before, does not appear to be a strict correlation between changes in K_{33}^T and change in k_p and d_{33} . Accordingly a more thorough study of poling behavior will be undertaken with the initial objective of uncovering any systematic correlation in the observed changes of those properties with poling.

V. RESPONSE TO HYDROSTATIC COMPRESSION

A number of ceramic discs of various compositions were subjected to hydrostatic pressure to determine its effect on their properties. The samples had aged for various times between 20 and 500 days before being subjected to compression. The samples were placed in closed rubber tubes, without having contact with each other, and stressed in an oil hydrostatic press. The pressure-time sequence used was the following:

13.79 MPa	2000 PSI	1 min
27.58	4000	1
41.36	6000	1
55.15	8000	1
68.94	10,000	5
55.15	8000	1
41.36	6000	1
27.58	4000	1
13.79	2000	1
0	0	2

where the times were those for which the given pressure was maintained. Pressures were changed manually in only a few seconds. This cycle was repeated 5 times.

The composition of the samples was as follows:

<u>Composition</u>	<u>Formula</u>
H-4	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.54}\text{Ti}_{.46})\text{O}_3 + 2.4 \text{ a/o Nb}$
H-7	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.52}\text{Ti}_{.48})\text{O}_3 + 2.4 \text{ a/o Sb}$
H-8	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.54}\text{Ti}_{.46})\text{O}_3 + 2.4 \text{ a/o Sb}$
H-9	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.56}\text{Ti}_{.44})\text{O}_3 + 2.4 \text{ a/o Sb}$
H-19	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.52}\text{Ti}_{.48})\text{O}_3 + 2.4 \text{ a/o Ta}$
H-20	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.54}\text{Ti}_{.46})\text{O}_3 + 2.4 \text{ a/o Ta}$
H-21	$\text{Pb}_{.95}\text{Sr}_{.05}(\text{Zr}_{.56}\text{Ti}_{.44})\text{O}_3 + 2.4 \text{ a/o Ta}$
29	$\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_{.53}\text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$
E	$\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_{.53}\text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985}$
E+	$\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_{.53}\text{Ti}_{.47})_{.997} \text{Fe}_{.003} \text{O}_{2.9985} + 1 \text{ w/o ZrO}_2$

The compositions identified by the letter H are of the type used in hydrophones and were discussed in the first Annual Summary Report⁽¹⁾. Composition 29 was made without putting the reactant powders through a blender. Powder E is the one described in Section II-B and E+ is powder E with zirconia added after the synthesis step.

The pre and post-compression data obtained are given in Table IX. They indicate that negligible changes occurred as a result of the compression. Also, data obtained at still later times shows that the compression treatment produced no discernable change in the aging rates of K_{33}^T or k_p at the time of its application.

These results are in agreement with those obtained by Palmer⁽⁹⁾, who subjected samples of 15 types of LZT (that differed either in the commercial supplier of the powder or sample, or in the composition) to ten cycles of compression up to 68.98 MPa (10,000 PSI) and made measurements after the 1st, 3rd, 6th and 10th compression. He found changes of about the magnitude reported here, with most of the change occurring during the first compression. He concluded that LZT ceramics are quite stable to this type of compression test, which simulates deep submergence.

VI. CONCLUSIONS AND FUTURE WORK

It is generally believed by commercial manufacturers of LZT piezo-electric ceramics that a "good" powder is required to make a "good" ceramic. The methods used to decide whether a powder is "good", and the specific powder preparation and firing techniques used are regarded as proprietary information. From information obtained by the Navy, however, it is known that the very same powder can be regarded as good by one manufacturer and bad by another⁽¹²⁾. This argues strongly that other factors besides the powder itself can have a profound effect on determining ceramic properties.

There is no way to characterize a powder as "good" or "bad" except by making a ceramic from it. This investigation has therefore been based on the development of a technique for making LZT powder which, by its nature, allows the presumption that the powder produced is both reacted and homogeneous to a high degree and therefore reproducible in its properties. The powder is still, however, primarily being judged on the basis of the behavior of ceramics made from it. This situation necessarily makes it difficult to draw firm conclusions about cause and effect relationships to ceramic properties. The following, however, represent the hypotheses on which future work will be based.

1. Powders made by the molten salt synthesis process are highly reacted and have excellent batch-to-batch reproducibility of their intrinsic properties.
2. The presence of zirconia in LZT powder, either as a result of incomplete reaction or introduced by ball wear during milling of the powder during its processing, has a deleterious effect on the dielectric constant and polarizability of ceramic fired from it.
3. The values of K_{33}^T , k_p and d_{33} obtained on poling a sample depend on its previous poling history as well as on the method used to produce the ceramic from the powder.
4. The aging of K_{33}^T is strongly influenced by other, presently unknown, factors besides domain randomization.
5. Cyclic application of hydrostatic pressure up to 69 MPa has little effect on the properties measured at atmospheric pressure or on the aging rate.

Further investigations under this contract will be directed primarily to studying the effect of various poling conditions and sample histories on the post-poling properties obtained in various compositions; and to studying the unusual aging behavior of K_{33}^T observed in the Cr containing compositions.

ACKNOWLEDGEMENT

The authors would like to express their appreciation to Dr. G. G. Palmer for graciously making available his long experience in commercial LZT manufacturing, to Mr. J. J. Jarek for making electrical measurements, and to Messrs. L. Ezrow and N. Cristello for ceramic fabrication and molten salt synthesis.

REFERENCES

1. "Lead Zirconate Titanate (LZT) Ceramics", Annual Summary Report, Contract N00014-76-C-0659, June 1977, Office of Naval Research.
2. "PbO Vapour Pressure in the $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ System", K. H. Hardtl and H. Rau, Solid State Comm. 7, pp. 41-45(1969).
3. "Point Defects and Sintering of Lead Zirconate-Titanate", R. B. Atkin and R. M. Fulrath, J. Am. Ceram. Soc. 54, pp. 265-270(1971).
4. Private Communication from Dr. Joseph Mazza, TAM Division of National Lead Industries, Niagara Falls, New York.
5. IRE Standards on Piezoelectric Crystals: Measurements of Piezoelectric Ceramics, 1961. Proc. IRE(Inst. Radio Engrs.), 49, pp. 1161-69(1961).
6. "Measurement of Particle Sizes in Opaque Bodies", R. L. Fullman, Trans. A.I.M.E., 197, 447(1953).
7. "Theory of the Dependence on Grain Growth During Intermediate-Stage Sintering", J. H. Rosolowski and C. Greskovich, J. Am. Ceram. Soc. 58, pp. 177-182(1975).
8. "The Grain-Size Dependence of the Electromechanical Properties in Lead Zirconate-Titanate Ceramics", A. H. Webster and T. B. Weston, Can. Ceram. Soc. J., 37, pp. XLI-XLIV(1968).
9. Private Communication from Dr. G. G. Palmer.
10. "Stabilization Effects in Piezoelectric Lead Zirconate Titanate Ceramics", H. Thomann, Ferroelectrics 4, pp. 141-146(1972).
11. "Piezoelectric Ceramics", B. Jaffe, W. R. Cook, Jr. and H. Jaffe, Academic Press, 1971, p. 160.
12. Private Communication from Dr. R. Pohanka, Naval Research Laboratory.

APPENDIX

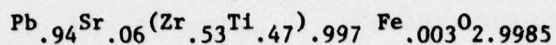
The recipe developed for producing LZT powder by the molten salt method follows. It can be scaled to make any desired quantity of product. The standard batch used in this work yielded 1 Kg of powder.

1. First, an aqueous slurry of the reactant compounds, typically oxides, hydroxides and carbonates, is prepared. Although the molten salt solvent provides an enhanced reaction condition, it is not able to completely overcome the inhomogeneities in a reaction mixture containing large, dense agglomerates of reactant material. To alleviate this problem, it has been found necessary to pass those reactants which contain these agglomerates through a brief, intense comminution process. It has been found that stirring an aqueous slurry of the powders for 60 seconds in a stainless steel food processing blender greatly alleviates this problem. The product of this comminution, usually the TiO_2 , ZrO_2 and any desired dopants, is added to the PbO . The quantity of PbO present is generally 2-10 wt.% in excess of that required for stoichiometry. Since PbO is soluble in dilute aqueous acetic acid, the excess PbO in the final product can be removed with an acid wash following the removal of the molten salt solvent by water washing.
2. Slurry the reaction mixture in H_2O at the rate of 1 l H_2O /1 kg reaction mixture. Vigorous stirring should be employed to obtain a complete suspension. Settled material will generally not react completely.
3. When a well mixed slurry is attained, continue stirring and add 0.454 kg/1 kg reactants of both $NaCl$ and KCl (0.908 kg total) as the solids.
4. Continue stirring until the mixture gels due to hydration (or carbonation) of the reactants. This gel will retain its homogeneity during subsequent processing.
5. Remove water by evaporation at $200^\circ C$ using suitable vessels, Teflon lined being best.

6. React the dried cake in either Pt, Pt lined or stabilized zirconia crucibles (covered) at 1000°C for 30 min to 1 hr in an air atmosphere, then cool at any convenient rate to room temperature.
7. Dissolve the NaCl-KCl from the reacted cake using distilled or deionized water. The solubility of the salt mixture is 0.5 kg/l of water at room temperature. Glass vessels and a motor driven stirrer are adequate to use. The brick-like cake will disintegrate into a fine powder that contains no perceptibly aggregated material.
8. The supernatant solution will have a high ionic strength which will cause the product powder to flocculate and settle when mixing is stopped. The supernatant can therefore be nearly quantitatively decanted to allow repeated washings with distilled water. Washing should be repeated until a stage is reached where the supernatant will remain milky white after about 10 min. of settling, indicating cessation of flocculation. At this point the residual chlorine ion concentration is low enough so as not to interfere with the next step.
9. Add enough concentrated acetic acid to make the slurry about 0.1M (4l, 1M CH_3COOH /1 kg product). Continue mixing for 30 to 60 min. The color of the product should lighten due to dissolution of the excess Pb added initially. Add an anionic flocculant (0.1 w/o aqueous solution of Hercafloc 821, Dupont Chemical Co.), allow the powder to settle and decant the liquid.
10. Repeat the acid treatment-flocculation-decantation twice.
11. Wash two more times during dilute acetic acid ($1 \times 10^{-3}\text{M}$). Use the minimum amount of flocculant necessary in steps 9, 10 and 11.
12. Dry the slurry by heating at 150°C.
13. The dried powder should be heated in air to about 500°C for about 20 min to remove any remaining water, acetic acid and flocculant. After this treatment it is ready to use.

TABLE I

PROPERTIES OF CERAMICS MADE FROM DIFFERENT POWDER BATCHES AND
FIRED AT THE SAME TIME IN A LARGE BOX FURNACE. POST-POLING VALUES
TAKEN AFTER 1 DAY. COMPOSITION OF CERAMICS:



Powder Batch	Density kg/m ³	K _O (1 KHz)	K ₃₃ ^T (1 KHz)	Tan Δ	k _p	d ₃₁ 10 ⁻¹² C/N
A	7.57 x 10 ³	931	1079	.0022	.350	-66
	7.57 x 10 ³	939	1084	.0021	.350	-66
	7.57 x 10 ³	934	1071	.0018	.334	-62
B	7.62 x 10 ³	983	1209	.0022	.498	-102
	7.58 x 10 ³	1002	1230	.0022	.502	-104
C	7.59 x 10 ³	971	1204	.0023	.483	-99
	7.58 x 10 ³	968	1209	.0024	.487	-100
	7.58 x 10 ³	971	1200	.0023	.478	-98
	7.59 x 10 ³	967	1198	.0026	.483	-99
D	7.59 x 10 ³	992	1243	.0024	.514	-109
	7.57 x 10 ³	989	1253	.0023	.518	-110
	7.57 x 10 ³	1029	1252	.0025	.521	-112
	7.59 x 10 ³	1038	1254	.0023	.518	-110
	7.59 x 10 ³	1029	1239	.0023	.522	-111
E	7.60 x 10 ³	1051	1265	.0024	.521	-111
	7.60 x 10 ³	1053	1258	.0024	.518	-110
	7.55 x 10 ³	1024	1253	.0024	.521	-111
	7.60 x 10 ³	1047	1260	.0026	.522	-111
	7.60 x 10 ³	1032	1274	.0025	.529	-114

TABLE II

PROPERTIES OF CERAMICS MADE FROM DIFFERENT POWDER BATCHES AND FIRED SEPARATELY IN A SMALL TUBE FURNACE. POST-POLING VALUES TAKEN AFTER 1 DAY. COMPOSITION OF CERAMICS: $\text{Pb}_{.94}\text{Sr}_{.06}(\text{Zr}_{.53}\text{Ti}_{.47})_{.997}\text{Fe}_{.003}\text{O}_{2.9985}$.

Powder Batch	Density Kg/m^3	K_o (1 KHz)	K_{33}^T (1 KHz)	Tan Δ	k_p	d_{31} 10^{-12} C/N	d_{33} 10^{-12} C/N
A	7.74×10^3	982	1093	.0023	.386	-72	192
	7.74×10^3	980	1087	.0024	.386	-72	189
	7.75×10^3	980	1076	.0021	.377	-69	181
	7.73×10^3	989	1085	.0023	.372	-69	171
B	7.74×10^3	1003	1113	.0025	.428	-82	216
	7.76×10^3	1003	1131	.0024	.460	-88	234
	7.76×10^3	1022	1153	.0024	.472	-92	243
	7.77×10^3	1016	1152	.0025	.476	-92	244
	7.76×10^3	1021	1135	.0024	.462	-89	235
C*	7.77×10^3	1038	1206	.0024	.498	-99	251
	7.74×10^3	1034	1208	.0024	.505	-101	258
	7.75×10^3	1050	1229	.0023	.515	-104	264
	7.73×10^3	1039	1233	.0022	.514	-104	264
	7.73×10^3	1041	1214	.0022	.511	-103	264
D	7.75×10^3	1030	1143	.0025	.439	-86	220
	7.72×10^3	1034	1180	.0025	.483	-96	246
	7.74×10^3	1034	1169	.0025	.472	-93	239
	7.71×10^3	1030	1168	.0025	.462	-91	227
E	7.78×10^3	1059	1229	.0023	.531	-108	270
	7.77×10^3	1050	1239	.0021	.524	-107	266
	7.77×10^3	1042	1205	.0024	.521	-105	264
	7.77×10^3	1058	1243	.0023	.518	-106	265

*Post-Poling Measurements Made After 2 Days.

TABLE III

PROPERTIES OF CERAMICS MADE FROM BATCH E POWDER TO WHICH
1 w/o ZrO_2 POWDER WAS ADDED AFTER SYNTHESIS. POST-POLING VALUES
TAKEN AFTER 1 DAY

Density Kg/m^3	K_o (1 KHz)	K_{33}^T (1 KHz)	$\tan \Delta$	k_p	d_{33} 10^{-12} C/N
7.59×10^3	966	1025	.0024	.338	177
7.60×10^3	972	1041	.0024	.344	178
7.64×10^3	976	1048	.0024	.357	188
7.60×10^3	975	1046	.0025	.353	187
7.62×10^3	975	1053	.0026	.362	195

TABLE IV

PROPERTIES OF CERAMICS FIRED FROM BATCH C POWDER IN A TUBE
FURNACE AT 1320°C. POST-POLING VALUES TAKEN AFTER 1 DAY

Atmosphere	Density Kg/m ³	K _o (1 KHz)	K ₃₃ ^T (1 KHz)	k _p
O ₂	7.70 x 10 ³	1000	1153	.485
O ₂	7.70 x 10 ³	988	1173	.496
O ₂	7.40 x 10 ³	950	1114	.464
O ₂	7.45 x 10 ³	964	1153	.477
O ₂	7.58 x 10 ³	960	1143	.478
Air	7.40 x 10 ³	950	1114	.464
Air	7.58 x 10 ³	960	1143	.478
Air	7.37 x 10 ³	966	1155	.474

TABLE V

AGING OF COMPOSITION 1. FIRED AT 1225°C.

SAMPLE DENSITY = $7.50 \times 10^3 \text{ Kg/m}^3$.

PRE-POLING DIELECTRIC CONSTANT = 865.

Days After Poling	K_{33}^T (1 KHz)	k_p	Tan Δ
1	1039	.425	
4	1027	.428	
6	1025	.424	
11	1019	.421	.0044
18	1010	.418	.0042
25	1011	.418	.0042
29	1008	.418	.0041
141	1029	.419	.0184
258	1900	.412	.3310
300	1457	.412	.2766
307	1489	.412	.2864
316	1329	.409	.2359
326	1244	.412	.2057
365	1184	.404	.1722
386	1149	.406	.1524
515	1583	.409	.3187

TABLE VI

AGING OF COMPOSITION 1. FIRED AT 1275°C.

SAMPLE DENSITY = $7.43 \times 10^3 \text{ Kg/m}^3$

PRE-POLING DIELECTRIC CONSTANT = 838.

Days After Poling	K_{33}^T (1 KHz)	k_p	Tan Δ
1	1025	.431	.0054
4	1017	.428	.0055
8	1009	.427	.0059
14	1008	.427	.0069
120	1159	.428	.1190
237	2457	.427	.5650
277	1399	.414	.2913
286	1564	.424	.3627
295	1349	.424	.2663
305	1261	.424	.2180
344	1177	.416	.1584
365	1138	.419	.1300

TABLE VII

AGING OF COMPOSITION 2. FIRED AT 1225°C.

SAMPLE DENSITY = $7.40 \times 10^3 \text{ Kg/m}^3$.

PRE-POLING DIELECTRIC CONSTANT = 805.

Days After Poling	K_{33}^T (1 KHz)	k_p	Tan Δ
1	908	.342	.0045
6	902	.341	.0038
11	901	.338	.0038
18	893	.337	.0036
25	897	.337	.0037
29	895	.337	.0037
39	894	.337	.0037
57	894	.337	.0037
88	894	.337	.0037
141	898	.338	.0058
244	1149	.331	.1257
258	1119	.334	.1139
298	990	.334	.1058
307	1030	.331	.1232
316	1029	.331	.1029
326	1067	.331	.0884
365	948	.327	.0763
386	934	.327	.0700
515	1075	.331	.1400

TABLE VIII

AGING OF COMPOSITION 2. FIRED AT 1275°C.

SAMPLE DENSITY = $7.40 \times 10^3 \text{ Kg/m}^3$.

PRE-POLING DIELECTRIC CONSTANT = 742.

Days After Poling	K_{33}^T (1 KHz)	k_p	Tan Δ
1	846	.341	.0042
4	846	.344	.0039
8	843	.341	.0038
14	841	.341	.0038
120	850	.341	.0088
237	943	.338	.0724
277	877	.324	.0422
286	893	.332	.0504
295	871	.334	.0389
305	867	.334	.0349
344	880	.324	.0281
365	873	.331	.0247
494	914	.334	.0594

TABLE IX
 PROPERTIES OF CERAMICS OF VARIOUS COMPOSITIONS BEFORE AND AFTER BEING SUBJECTED
 TO 5 CYCLES OF COMPRESSION TO 68.98 MPa. UNITS OF d_{33} ARE 10^{-12} C/N.
 DIELECTRIC CONSTANTS MEASURED AT 1 KHz.

Composition	Before Compressing			2 Hours After			2 Days Later		
	d_{33}	K_{33}^T	k_p	d_{33}	K_{33}^T	k_p	d_{33}	K_{33}^T	k_p
H-4	307	1628	.472	309	1657	.476	310	1635	.476
H-4	294	1483	.474	293	1513	.479	296	1481	.478
H-4	299	1588	.504	302	1600	.502	304	1585	.504
H-7	170	1194	.300	170	1221	.303	171	1196	.303
H-8	259	1639	.380	263	1693	.386	264	1643	.383
H-9	140	901	.253	142	934	.248	143	903	.253
H-19	144	1048	.262	144	1063	.262	145	1049	.262
H-20	297	1452	.509	300	1472	.507	304	1451	.509
H-21	226	772	.452	223	787	.449	226	772	.452
29	246	1151	.495	247	1155	.504	250	1150	.504
E	246	1143	.498	248	1147	.498	248	1141	.498
E+	166	966	.324	161	972	.324	165	957	.324

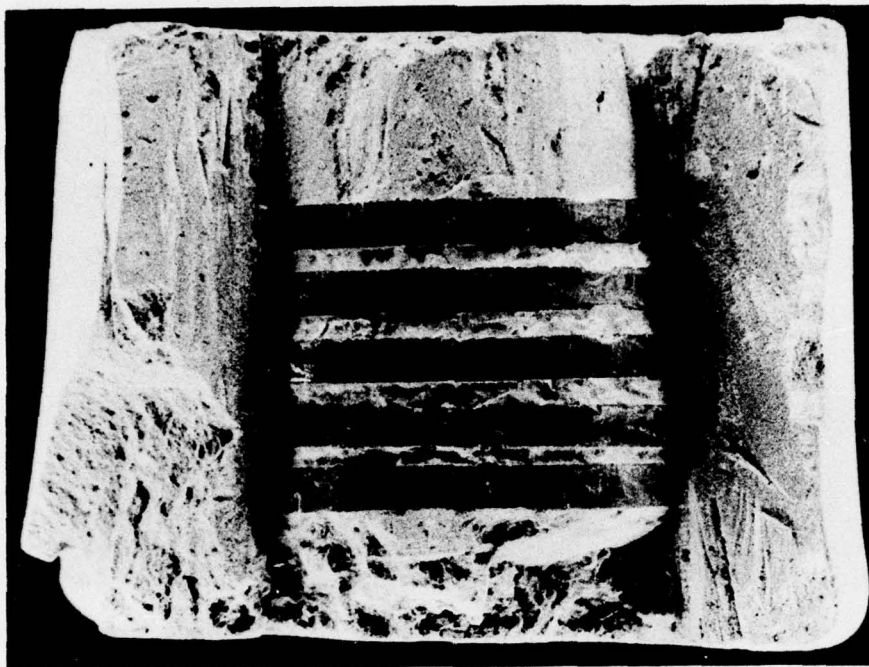


Figure 1. Sintered Sample Discs and Surrounding, Lightly Sintered Powder as Removed from Crucible. 3.5X.

PRECEDING PAGE BLANK

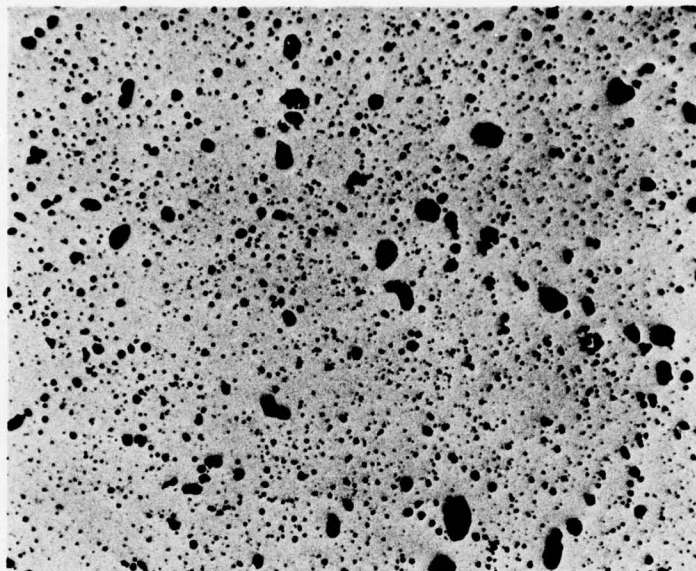


Figure 2a. Polished Surface of Ceramic Made from Batch C Powder Fired in Box Furnace. 50X.

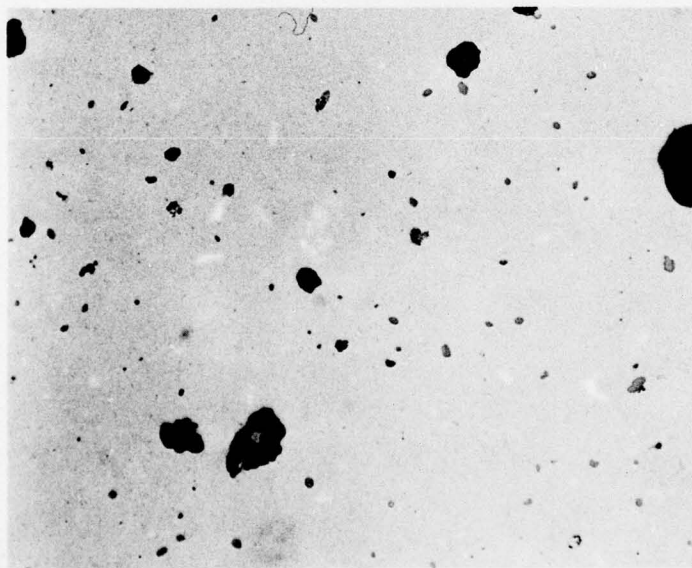


Figure 2b. Polished Surface of Ceramic Made from Batch C Powder Fired in Box Furnace. 500X.

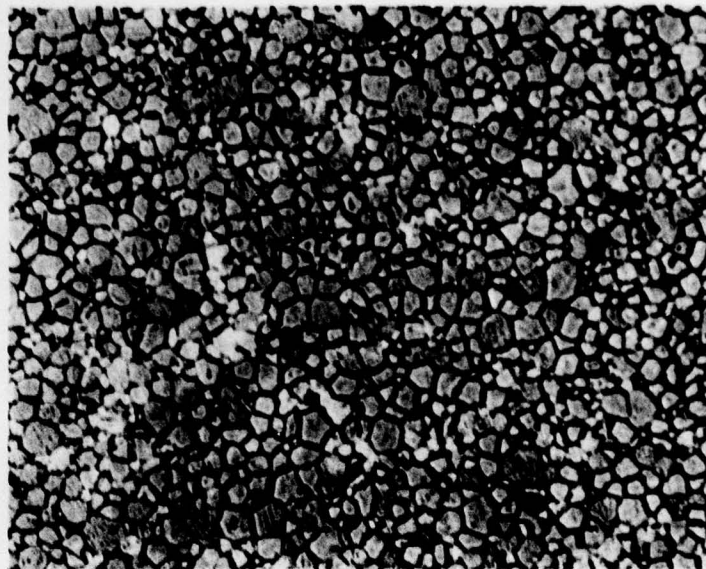


Figure 2c. Polished and Etched Surface of Ceramic Made
from Batch C Powder Fired in Box Furnace. 1000X.

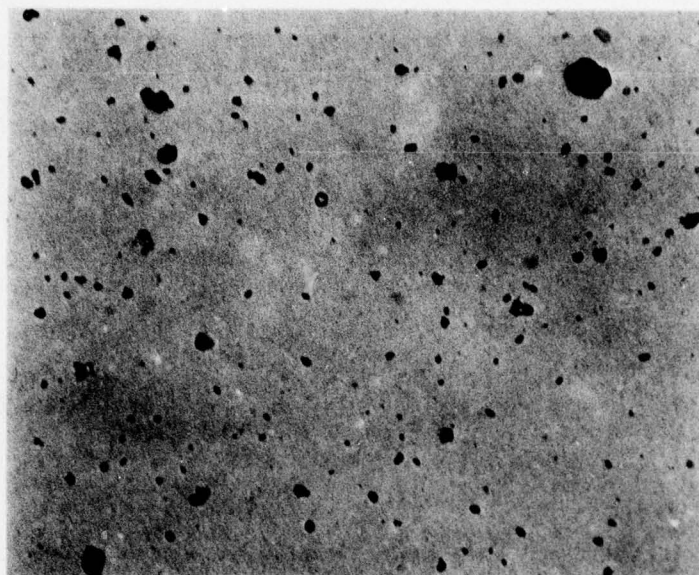


Figure 3. Polished Surface of Ceramic Made from Batch A Powder and Fired in Box Furnace. 500X.

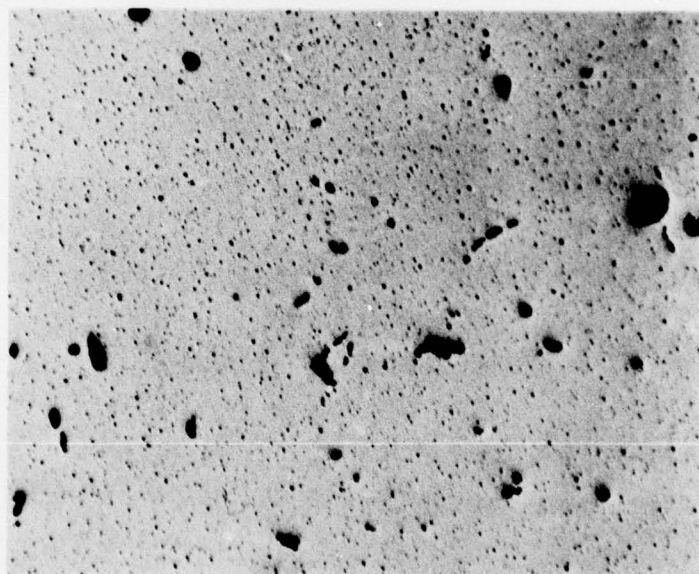


Figure 4a. Polished Surface of Ceramic Made from Batch C Powder and Fired in Tube Furnace. 50X.

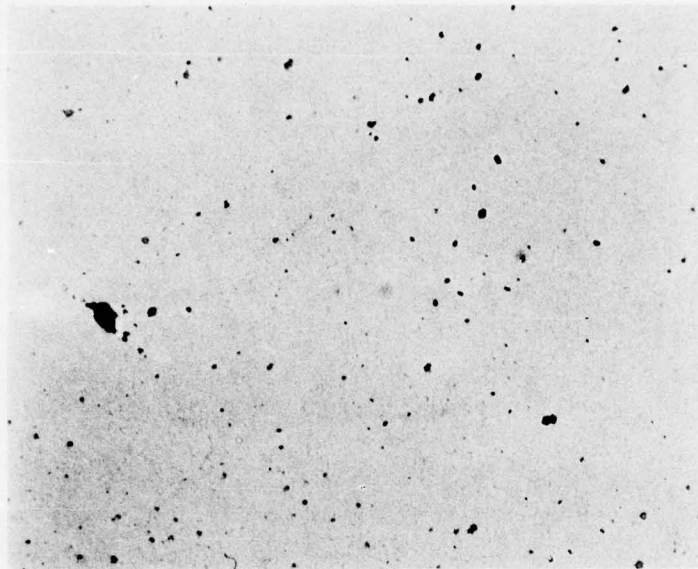


Figure 4b. Polished Surface of Ceramic Made from Batch C Powder and Fired in Tube Furnace. 500X

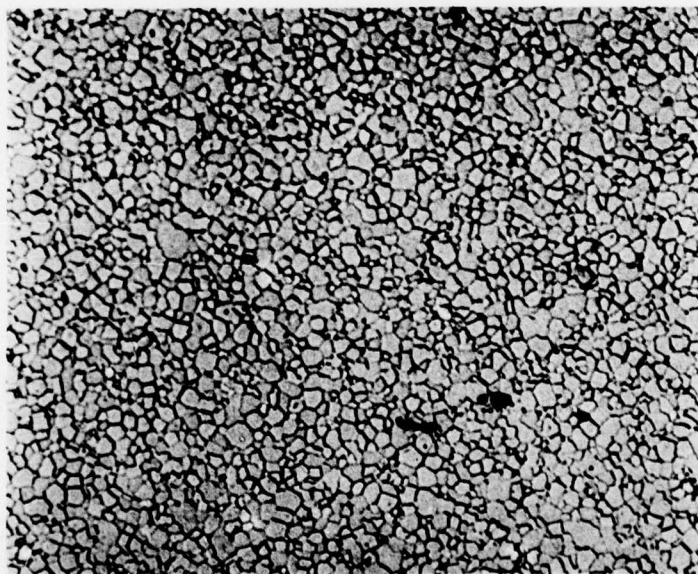


Figure 4c. Polished and Etched Surface of Ceramic Made from Batch C Powder and Fired in Tube Furnace. 1000X.

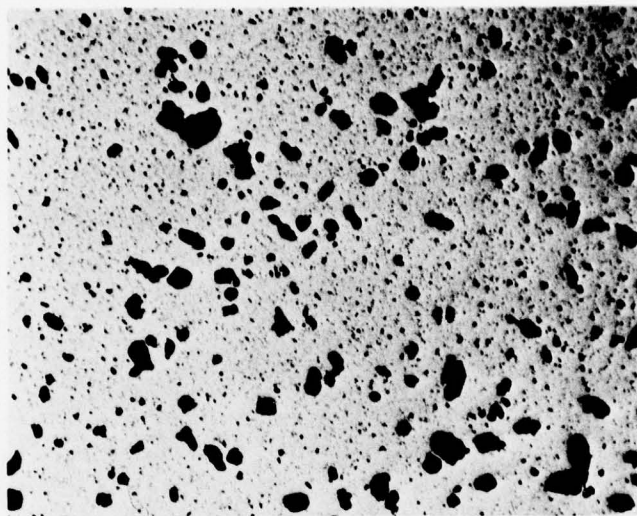


Figure 5a. Polished Surface of Ceramic Made from Batch E Powder +1 w/o ZrO_2 and Fired in Tube Furnace. 50X.

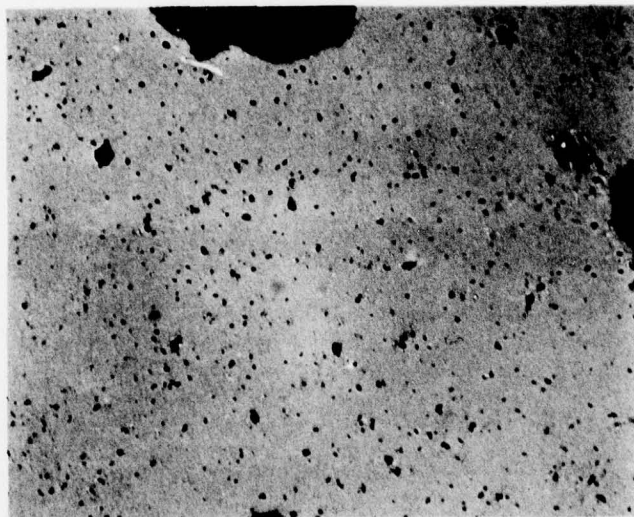


Figure 5b. Polished Surface of Ceramic Made from Batch E Powder +1 w/o ZrO_2 and Fired in Tube Furnace. 500X.

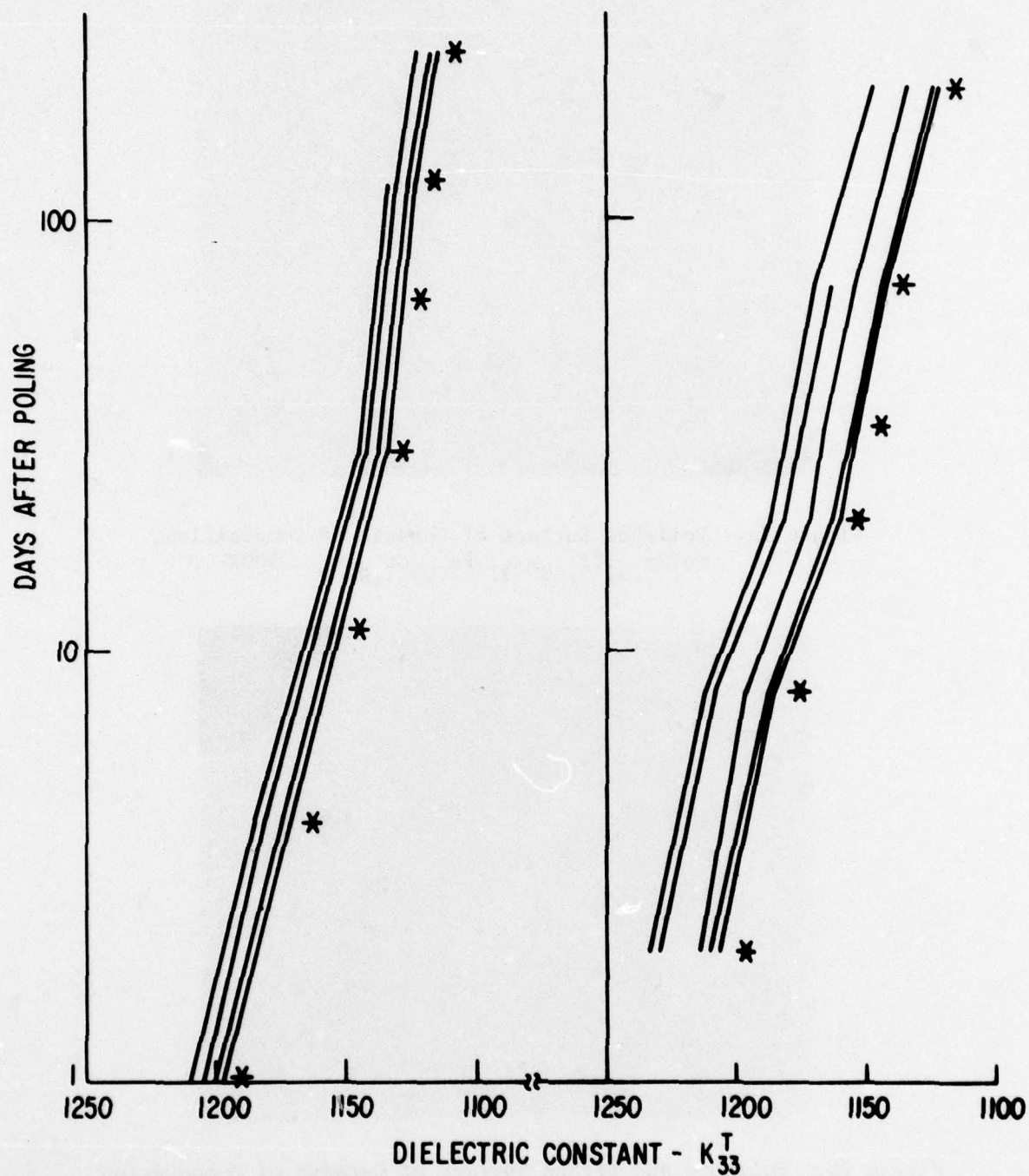


Figure 6. Aging of Dielectric Constant of Samples Made from Powder Batch C and Fired in: (a), Box Furnace; (b), Tube Furnace

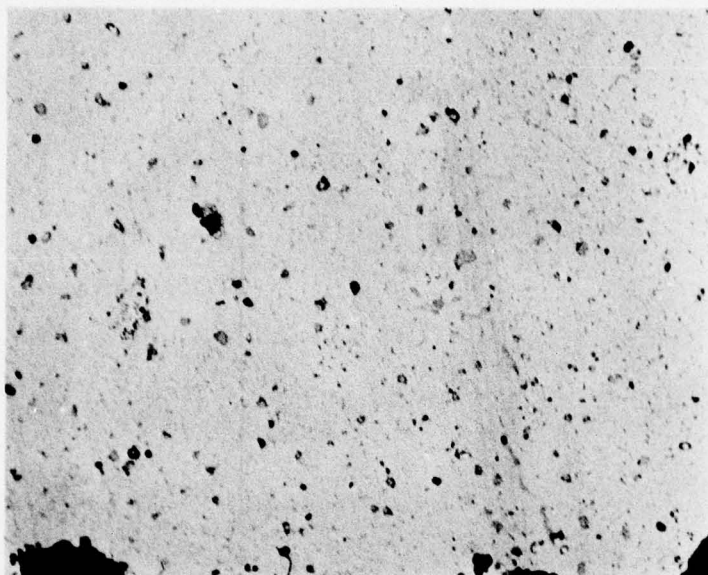


Figure 7a. Polished Surface of Ceramic of Composition,
 $\text{Pb}(\text{Zr}_{.52}\text{Ti}_{.48})_{.97}\text{Fe}_{.01}\text{Cr}_{.02}\text{O}_3$. 500X.

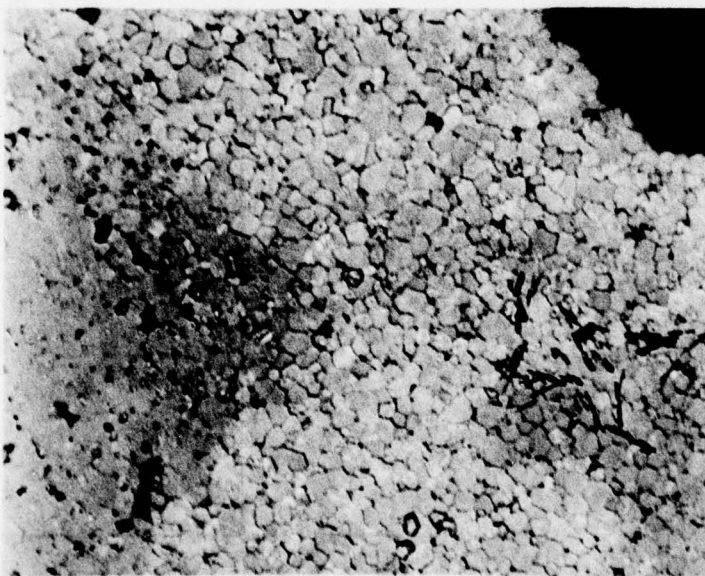


Figure 7b. Polished and Etched Surface of Ceramic of Composition
 $\text{Pb}(\text{Zr}_{.52}\text{Ti}_{.48})_{.97}\text{Fe}_{.01}\text{Cr}_{.02}\text{O}_3$. 1000X.

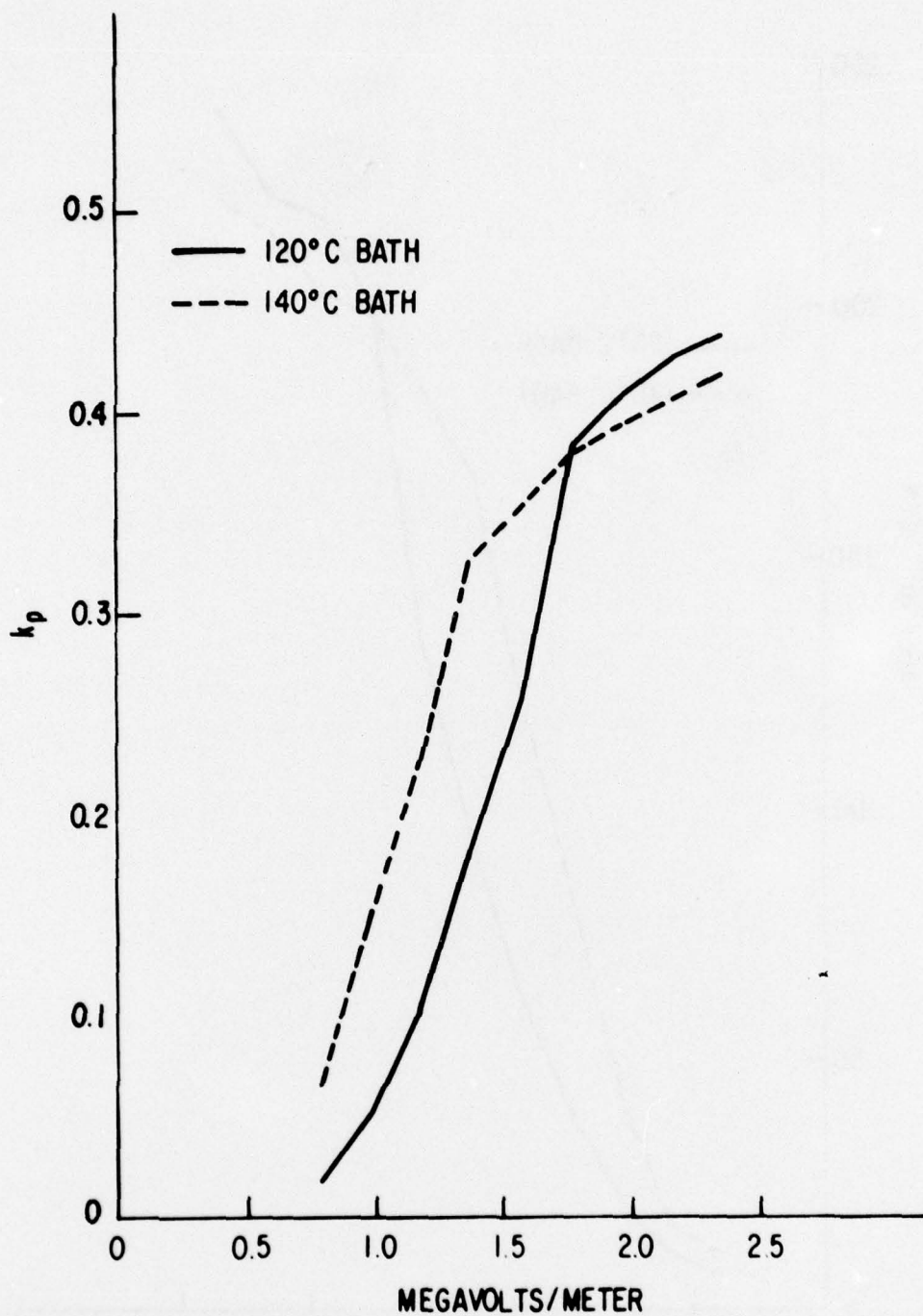


Figure 8. Variation of Planar Coupling Coefficient with Poling Field for Two Poling Temperatures

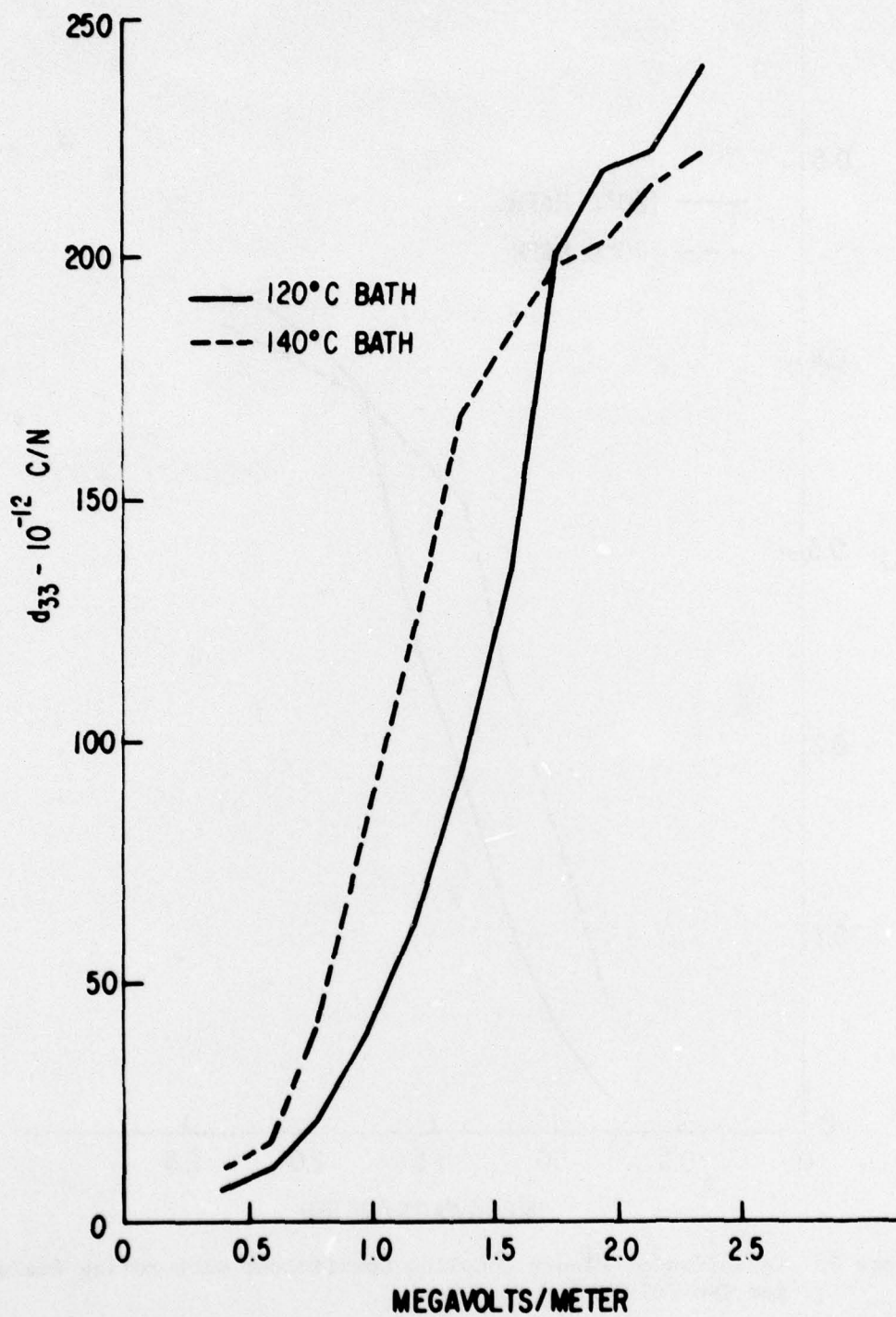


Figure 9. Variation of Piezoelectric Strain Constant, d_{33} , with Poling Field for Two Poling Temperatures

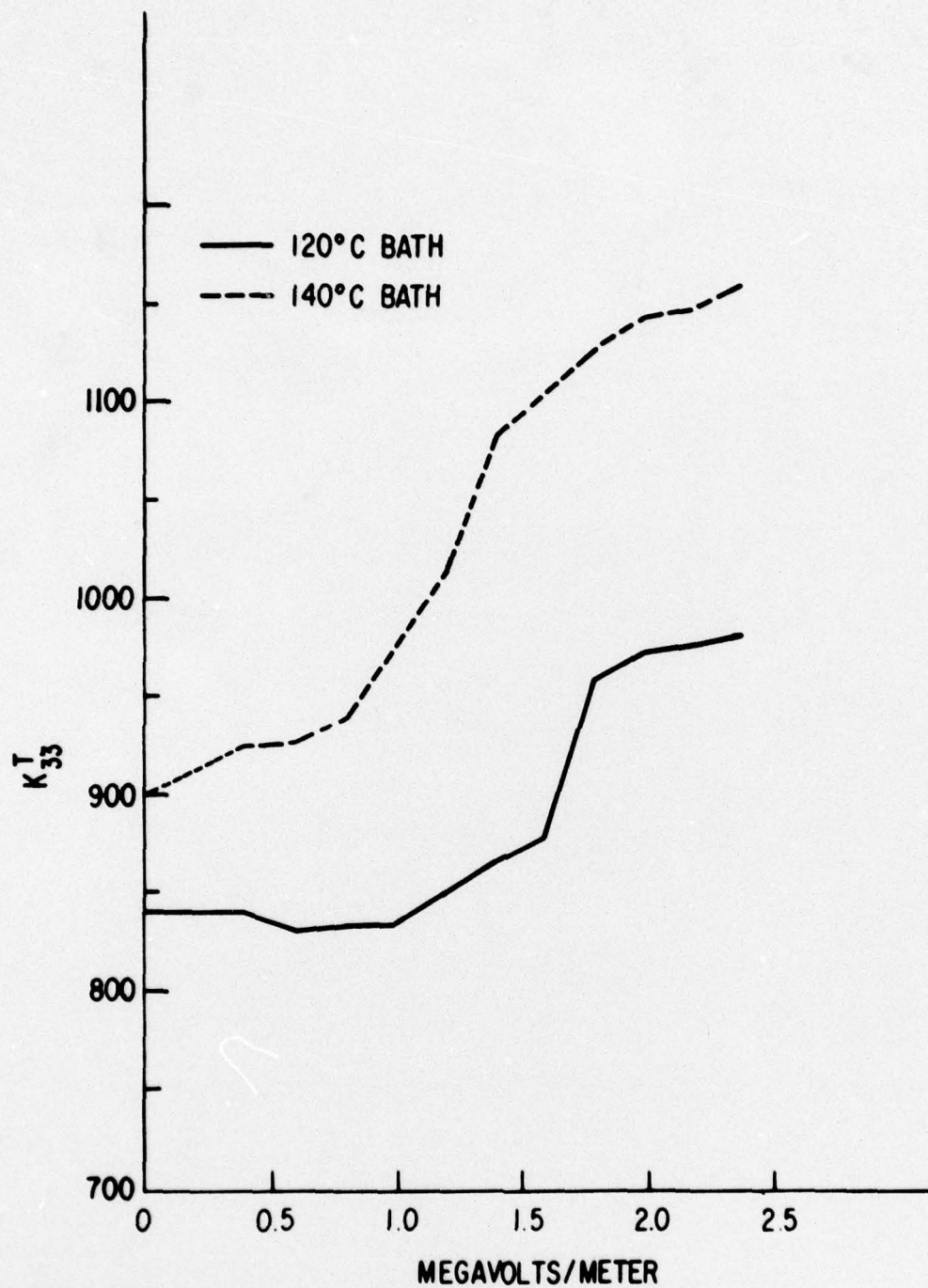


Figure 10. Variation of Dielectric Constant at 1 kHz with Poling Field for Two Poling Temperatures